Linear and nonlinear superparamagnetic relaxation at high anisotropy barriers

Yu.L. Raikher* and V.I. Stepanov

Institute of Continuous Media Mechanics, Ural Division of RAS, 614013, Perm, Russia

The micromagnetic Fokker-Planck equation is solved for a uniaxial particle in the low-temperature limit. Asymptotic series in the parameter that is the inverse barrier height–to–temperature ratio are derived. With the aid of these series, the expressions for the superparamagnetic relaxation time and the odd-order dynamic susceptibilities are presented. The obtained formulas are both quite compact and practically exact in the low (with respect to FMR) frequency range that is proved by comparison with the numerically-exact solution of the micromagnetic equation. The susceptibilities formulas contain angular dependencies that allow to consider textured as well as randomly oriented particle assemblies. Our results advance the previous two-level model for nonlinear superparamagnetic relaxation.

PACS numbers: 75.30.Cr, 75.30.Gw, 75.50.Tt

I. INTRODUCTION

The problem of superparamagnetic relaxation in single-domain ferroparticles formulated, explained and basically analyzed by Néel[1] about fifty years ago, since then keeps to attract attention. Nowadays this interest is mainly due to the expanding number of nanometer granular magnetic media used in information storage and related high technologies.

When analyzing magnetic dispersions, solid or fluid, a promising idea is to evaluate the granulometric content, particle material parameters and relaxation rates by combining the data on linear and nonlinear dynamic susceptibilities. Since recently, this approach (it originates from the spin glass science) became quite feasible in experimental realization.[2] However, to benefit from it, one needs an adequate model. Surprisingly, until nowadays the Néel[1] concept of superparamagnetic behavior of fine magnetic particles that had been substantially advanced by Brown[3, 4] and refined by numerous researchers (see the review article[5] with about 400 references), lacks a nonlinear extension.

In Ref. 6 we begun to fill up this gap and proposed a numerical procedure involving continuous fractions by means of which the linear and cubic susceptibilities for a solid system of uniaxial fine particles could be obtained. With allowance for the polydispersity of real samples, the worked out description provided a fairly good agreement with the dynamic magnetic measurements taken on Co-Cu nanocomposites.[2] Recently, our approach was used successfully[7] for the linear and cubic susceptibilities of the samples of randomly oriented γ-Fe_2O_3 nanoparticles. Hereby we carry on the build-up of the nonlinear superparamagnetic relaxation theory by working out a set of compact and accurate analytical expressions that considerably facilitate calculations as well as experiment inter-pretation.

The paper is arranged in the following way. In Sec. II we discuss the problem of superparamagnetic relaxation and show the way to obtain the asymptotic solution for the micromagnetic Fokker-Planck equation in the uniaxial case. In Sec. III the perturbative expansions for the orientational distribution function are obtained, which are used in Sec. IV to construct asymptotic expressions for the nonlinear dynamic susceptibilities. The explicit forms of those expansions are given and their accuracy is proved by comparison with the results of numerical calculations. Sec. V contains the enveloping discussion.

II. SUPERPARAMAGNETIC RELAXATION TIMES

A. Uniaxially anisotropic particle

The cornerstone of the superparamagnetic relaxation theory is the Arrhenius-like law for the relaxation rate of a magnetic moment of a single domain particle predicted by Néel in 1949. The framework of this classical problem is as follows. Consider an immobile (e.g. fixed inside a solid matrix) single-domain grain of a volume v. This particle possesses a uniaxial volume magnetic anisotropy, K being its energy density and $\boldsymbol{n}$ its easy axis direction. Since the temperature T is assumed to be much lower than the Curie point, the particle magnetization I, as a specific parameter, is practically constant and the magnitude of the particle magnetic moment may be written as $\mu = Iv$. Denoting its direction by a unit vector $\boldsymbol{e}$, one concludes that the magnetic state of such a particle is exhaustively characterized by a pair of vectors: $\boldsymbol{\mu} = Iv\boldsymbol{e}$ and $\boldsymbol{n}$. Thence, the orientation-dependent part of the particle energy (in the absence of external magnetic fields) is

$$U = -Kv(\boldsymbol{e} \cdot \boldsymbol{n})^2, \qquad (1)$$

where K is assumed to be positive. As Eq. (1) shows, this energy has two equal minima. They are separated

---

*Corresponding author. Fax: +7 (3422) 336957; e-mail: raikher@icmm.ru

by the potential barrier of the height Kv and correspond to $e \parallel \pm n$ because for the magnetic moment e the directions n and $-n$ are equivalent. At zero temperature, the magnetic moment e, once located in a particular potential well, is confined there forever. At finite temperature, the probability of an overbarrier (interwell) transition becomes non-zero. If the ratio $\sigma \equiv Kv/kT$ is high enough, the transition rate is exponential thus yielding the Néel law $\tau \propto \exp(\sigma)$ for the reference time τ of the particle re-magnetization.

Brown[4] shaped up those semi-qualitative considerations into a rigorous Sturm-Liouville eigenvalue problem by deriving the micromagnetic kinetic equation

$$2\tau_D \, \partial W/\partial t = \widehat{\boldsymbol{J}} W \widehat{\boldsymbol{J}} (U/kT + \ln W), \qquad (2)$$

where $W(e, t)$ is the orientational distribution function of the magnetic moment, $\widehat{\boldsymbol{J}} = (e \times \partial/\partial e)$ is the infinitesimal rotation operator with respect to e, and the time τ_D is introduced below by formula (4). Generally speaking, equation (2) is incomplete since a gyromagnetic term is absent there. This means that the consideration is limited by the frequency range $\omega \tau_0 \ll 1$, where τ_0 is the relaxation time of the Larmor precession of the particle magnetic moment in the internal anisotropy field $H_a \sim = 2K/I$, where K includes the possible shape contribution. Comparing this condition with the other one, $\omega_L \tau_0 \lesssim 1$, that evidences a low-to-moderate quality factor of the Larmor precession for real nanodisperse ferrites, one estimates the allowed frequency as $\omega \ll \omega_L$ that means, in fact, a fairly wide range.[25]

In the statistical description delivered by Eq. (2), the observed (macroscopic) magnetic moment per particle is given by the average

$$\boldsymbol{m}(t) = \mu \langle \boldsymbol{e} \rangle = \int \boldsymbol{e} \, W(\boldsymbol{e}, t) \, d\boldsymbol{e}, \qquad (3)$$

Note that with allowance for Eq. (1) the function W has a parametric dependency on the vector n so that, in fact, the angular argument of W is $(e \cdot n)$.

The magnetodynamic equation underlying the Brown kinetic equation (2) can be either that by Landau & Lifshitz or that by Gilbert. To be specific, we adopt the former one. Thence, the reference relaxation time in Eq. (2) writes as

$$\tau_D = Iv/2\alpha\gamma kT, \qquad (4)$$

where γ is the gyromagnetic ratio for electrons and α is the precession damping (spin-lattice relaxation) phenomenological parameter.

Assuming uniaxial symmetry of the time-dependent solution and separating the variables in Eq. (2) in the form

$$W(\boldsymbol{e}, t) = \tfrac{1}{2\pi} \sum_{\ell=0}^{\infty} A_\ell \, \psi_\ell(\boldsymbol{e} \cdot \boldsymbol{n}) \, \exp(-\lambda_\ell t/2\tau_D), \quad (5)$$

where the amplitudes A_ℓ depend on the initial perturbation, one arrives at the spectral problem

$$\widehat{L}\psi_\ell = \lambda_\ell \psi_\ell, \qquad \widehat{L} \equiv \widehat{\boldsymbol{J}}\Big[2\sigma(\boldsymbol{e}\cdot\boldsymbol{n})(\boldsymbol{e}\times\boldsymbol{n}) - \widehat{\boldsymbol{J}}\Big], \quad (6)$$

where the non-negativity of the decrements λ_ℓ can be proven easily. Expanding the eigenmodes ψ_ℓ in the Legendre polynomial series

$$\psi_\ell = \tfrac{1}{2} \sum_{k=1}^{\infty} (2k+1)\, b_k^{(\ell)} P_k(\cos\theta), \quad k = 1, 3, 5, \dots, \ (7)$$

where θ is the angle between e and n, one arrives at the homogeneous tridiagonal recurrence relation

$$\left[1 - \frac{\lambda_\ell}{k(k+1)}\right] b_k^{(\ell)} - 2\sigma \left[\frac{k-1}{(2k-1)(2k+1)} \, b_{k-2}^{(\ell)} + \frac{1}{(2k-1)(2k+3)} \, b_k^{(\ell)} - \frac{k+2}{(2k+1)(2k+3)} \, b_{k+2}^{(\ell)}\right] = 0, \qquad (8)$$

Note that Eqs. (5)–(8) describe only the longitudinal (with respect to the easy axis) relaxation of the magnetic moment. We remark that under condition $\omega \ll \omega_L$, i.e., far from the ferromagnetic resonance range, the transversal components of $\boldsymbol{m} = \mu \langle \boldsymbol{e} \rangle$ are of minor importance.

B. Interwell mode

Spectral equation (6) describes the temperature-induced (fluctuation) motions of the vector e in the orientational potential with a symmetrical profile (1). With respect to the time dependence, the set of possible eigenmodes splits into two categories: interwell (overbarrier) transitions and intrawell wanderings. In the spectral problem (6) the interwell transitions of the magnetic moment are associated with the single eigenvalue λ_1. As the rigorous analysis shows,[8] it drastically differs from the others: whereas for $\ell \geq 1$ all the λ_ℓ gradually *grow* with σ, the decrement λ_1 exponentially *falls down* proportionally to $\exp(-\sigma)$.

In the opposite limit $\sigma \to 0$, all the decrements, including λ_1, tend to the sequence $\lambda_\ell = \ell(\ell+1)$ and thus become of the same order of magnitude. This regime corresponds to a vanishing anisotropy so that the difference between the inter- and intrawell motions disappear,

and the magnetic moment diffuses almost freely over all the 4π radians with the reference time τ_D introduced by Eq. (4).

From Eqs. (3) and (5) one finds that the longitudinal component of the magnetic moment evolves according to

$$m(t) = \mu \sum_{\ell=1}^{\infty} A_\ell \, e^{-\lambda_\ell t/2\tau_D} \int_{-1}^{1} x\psi_\ell \, dx, \qquad (9)$$

where $x = \cos\theta = (\boldsymbol{e} \cdot \boldsymbol{n})$. For a symmetrical potential like (1) the equilibrium value m_0 of the particle magnetic moment is zero.

With the above-mentioned structure of the eigenvalue spectrum, the term with $\ell = 1$ in Eq. (9), being proportional to $\exp(-e^{-\sigma}t/\tau_D)$, at $\sigma > 1$ is far more long-living than any other one. The dominating rôle of the decrement λ_1 had been proven by Brown, and for it he had derived[4] the asymptotic expression

$$\lambda_\mathrm{B} = (4/\sqrt{\pi}) \, \sigma^{3/2} \, e^{-\sigma}, \qquad (\sigma \gg 1). \qquad (10)$$

In a short time after, using a continued fraction method, Aharoni constructed[9] for λ_1 a fairly long power series in σ and also showed numerically that Brown's expression (10) resembles the exact one with the accuracy of several percent for $\sigma \gtrsim 3$. In the 90's the eigenvalue λ_1 became a subject of extensive studies. Efficient numerical procedures were developed [10] and a number of extrapolation formulas with a good overall accuracy were proposed[11, 12, 13, 14].

C.   Asymptotic solution of the Brown equation

The study that we describe below was inspired by our work on fitting the dynamic susceptibilities measurements for real assemblies of fine particles. Those data typically describe polydisperse systems in the low-frequency bandwidth $\omega/2\pi = 1$–10^3 Hz. As $\tau_0 \sim 10^{-9}$ s or smaller, then, using formula (10) for estimations, one concludes that the mentioned frequency interval becomes a dispersion range for the interwell (superparamagnetic) mode at

$$\omega\tau_0 e^\sigma \gtrsim 1 \quad \text{that is} \quad \sigma \gtrsim 10.$$

For temperatures up to 300 K this condition holds for quite a number of nanomagnetic systems.

Application of the best fit procedure to a set of experimental data implies numerous re-calculations of the linear and non-linear susceptibility curves $\chi^{(k)}$ of the assembly. Any such curve, due to a considerable polydispersity of the particles, is a superposition of a great number of partial curves $\chi^{(k)}(\sigma)$ spread over a wide size (or, in the dimensionless form, σ) range. For successful processing, one needs a fast and very accurate algorithm to evaluate $\chi^{(k)}(\sigma)$ everywhere including the domain $\sigma \gg 1$. The existing extrapolation formulas are no good for that purpose due to their ill-controllable error accumulation. A plausible way out is an asymptotic in σ^{-1} solution of Eq. (6). In the course of the fitting procedure, this approximation can be easily matched in the intermediate σ range with the well-known expansions for the small σ end.

It is noteworthy that some 20 years ago Brown himself resumed[15, 16] studies on λ_1 and modified the pre-exponential factor in Eq. (10) transforming it into an asymptotic series in σ^{-1}. On the base of Eq. (6) he had constructed an integral recurrence procedure, and evaluated λ_1 down to terms $\propto 1/\sigma^{10}$. What we do below, is, in fact, carrying on this line of analysis that had not been touched since then. Our method advances Brown's results in two aspects. First, for λ_1 it is more simple. Second, it provides not only the eigenvalue but the eigenfunction as well. Only having the latter in possession, one is able to obtain theoretical expressions for the directly measurable quantities that is the susceptibilities $\chi^{(k)}$.

Taking Eq. (6) as the starting point, we remark its equilibrium solution

$$\psi_0 = Z_0^{-1} \exp(\sigma x^2), \quad Z_0 = 2R(\sigma), \qquad (11)$$
$$R(\sigma) = \int_0^1 \exp(\sigma x^2) \, dx,$$

that corresponds to $\ell = 0$ and $\lambda_0 = 0$ and note the asymptotic expansion for the partition integral $R(\sigma)$ found in Ref. 17:

$$R(\sigma) = e^\sigma G/2\sigma, \quad G(\sigma) \equiv 1 + \frac{1}{2\sigma} + \frac{3}{4\sigma^2} + \frac{15}{8\sigma^3} + \ldots + \frac{(2n-1)!!}{2^n\sigma^n} + \ldots. \qquad (12)$$

The operator $\widehat{L}$ in Eq. (6) is not self-conjugated and thus produces two sets of eigenfunctions, which obey the respective equations

$$\widehat{L}\psi_k = \lambda_k\psi_k, \qquad \widehat{L}^+\varphi_j = \lambda_j\varphi_j; \qquad (13)$$

here + denotes Hermitian conjugation. The eigenfunctions of these two families are orthonormalized and related to each other in a simple way:

$$\psi_k = \psi_0 \varphi_k\,, \qquad \int_{-1}^{1} dx\, \varphi_j \psi_k = \delta_{jk}\,. \qquad (14)$$

Qualitatively, from Eq. (14) one may say that φ_k are the same eigenfunctions but "stripped" of the exponential equilibrium solution ψ_0. Substituting Eq. (14) in Eq. (6), one gets two useful relationships

$$-\widehat{\boldsymbol{J}}\psi_0\widehat{\boldsymbol{J}}\varphi_k = \lambda_k \psi_0 \varphi_k, \qquad \int \psi_0(\widehat{\boldsymbol{J}}\varphi_j)(\widehat{\boldsymbol{J}}\varphi_k)\,dx = \lambda_k \delta_{jk}\,, \qquad (15)$$

where the second one follows from the first after multiplication by φ_i and integration by parts. Note that in the second formula action of each operator reaches no farther than the nearest closing parenthesis.

On rewriting Eq. (15.1) in terms of a single orientational variable $x = (\boldsymbol{e}\cdot\boldsymbol{n})$, the spectral problem takes the form

$$\frac{d}{dx}\left[\psi_0(1 - x^2)\frac{d\varphi_k}{dx}\right] = -\lambda_k \psi_0 \varphi_k. \qquad (16)$$

In the equilibrium state Eq. (16) reduces to

$$\frac{d}{dx}\left[\psi_0(1 - x^2)\frac{d\varphi_0}{dx}\right] = 0, \qquad (17)$$

whose normalized solution is $\varphi_0 = 1$. This solution, being a true equilibrium one, turns the inner part of the brackets, i.e., the probability flux in the kinetic equation (2), into identical zero.

As remarked in Sec. II B, at $\sigma \gg 1$ the most long-living non-stationary solution of Eq. (16) is the eigenfunction with $\ell = 1$, whose eigenvalue is exponentially small, see Brown's estimation (10). We use this circumstance for approximate evaluation of φ_1 in the $\sigma \gg 1$ limit by neglecting the right-hand side of Eq. (16) for $\ell = 1$. On doing that, the equation obtained for the function φ_1 formally coincides with equation (17) for φ_0. However, the essential difference is that now the content of the bracket is non-zero:

$$\psi_0(1 - x^2)\frac{d\varphi_1}{dx} = \tfrac{1}{2}C, \qquad (18)$$

where $\tfrac{1}{2}C$ is the integration constant. Note also that, contrary to φ_0, the sought for solution φ_1 is odd in x.

Using the explicit form of ψ_0 from Eq. (11) and integrating, one gets for $x > 0$

$$\varphi_1 = CR\int_0^x \frac{e^{-\sigma x^2}}{1 - x^2}\,dx = CR\int_0^x e^{-\sigma x^2}\left(1 + x^2 + x^4 + x^6 + \ldots\right)dx. \qquad (19)$$

The integrals in expansion (19) are akin. Denoting

$$F_n = \int_0^x x^{2n}\,e^{-\sigma x^2}\,dx,$$

one can easily write for them the recurrence relation and "initial" condition as

$$F_n = -\frac{\partial}{\partial\sigma}F_{n-1}\,, \qquad F_0 = \frac{\sqrt{\pi}}{2\sqrt{\sigma}}\,\text{erf}(\sqrt{\sigma}x), \qquad (20)$$

respectively. Using the asymptotics of the error integral, with the exponential accuracy in σ one finds

$$F_n = [(2n - 1)!!/2^n\sigma^n]\,F_0\,, \qquad F_0 \simeq \sqrt{\pi}/2\sqrt{\sigma}. \qquad (21)$$

Comparing this with expression (12) for the function G, we get the representation

$$\varphi_1(x > 0) \simeq CRF_0G. \qquad (22)$$

Applying to Eq. (22) the normalizing condition (14), one evaluates the constant as $C = 1/RF_0G$. Therefore, from

Eqs. (20)–(22) the principal relaxational eigenmode determined with the $\exp(-\sigma)$ accuracy emerges as an odd step function

$$\varphi_1(x) \simeq \begin{cases} -1 & \text{for } x < 0, \\ 1 & \text{for } x > 0. \end{cases} \qquad (23)$$

In Fig. 1 the limiting contour (23) is shown against the exact curves $\varphi_1(x)$ obtained by solving numerically Eq. (8) for several values of σ. We remark that in the statistical calculations carried out below the typical integrals are of two kinds. In the first, the integrand consists of the product of $\varphi_1\psi_0$ and some non-exponential function. As $\psi_0 \propto \exp\sigma x^2$, the details of behavior of φ_1 in the vicinity of $x = 0$ are irrelevant because the approximate integral will differ but exponentially from the exact result. The integrals of the second type contain $d\varphi_1/dx$ in the integrand. For them a step-wise approximation Eq. (23) with its derivative equal identical zero everywhere except for $x = 0$ is an inadmissible choice. So, to keep the exponential accuracy in this case, one has to get
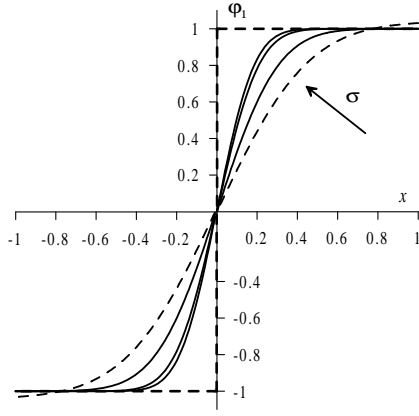
FIG. 1: Eigenmode $\varphi_1(x)$ determined with the aid of the numerical solution of Eq. (8) for the dimensionless barrier height σ: 5 (dashed line), 10, 20, 25 (solid lines); the arrow shows the direction of σ growth. Thick dashes show the step-wise function that is the limiting contour for φ_1 at $\sigma \to \infty$.

FIG. 2: Asymptotic expression (25) for the eigenvalue λ_1 with allowance for terms up to σ^{-9} (solid line) compared to the exact numeric value (dashed line).

back to Eq. (18).

The eigenvalue λ_1 corresponding to the approximate eigenfunction φ_1 from Eq. (23) is evaluated via formula (15) that can be rewritten as

$$\lambda_1 = \int_{-1}^{1} \psi_0 \left(\widehat{\boldsymbol{J}}\varphi_1\right)^2 = \frac{1}{R} \int_0^1 e^{\sigma x^2} (1-x^2) \left(\frac{d\varphi_1}{dx}\right)^2 dx. \tag{24}$$

Substituting the derivative from Eq. (18), one finds

$$\lambda_1 = C = (2/\sqrt{\pi})\, \sigma^{1/2}/RG,$$

and using expression (12) for R finally arrives at

$$\lambda_1 = (4/\sqrt{\pi})\, \sigma^{3/2} e^{-\sigma}/G^2 = \lambda_{\mathrm{B}}/G^2. \tag{25}$$

With G expanded in powers of σ^{-1}, see Eq. (12), this formula reproduces the asymptotic expression derived by Brown in Ref. 15. At $G = 1$ it reduces to his initial result,[4] corresponding to the above-given Eq. (10). Function $\lambda_1(\sigma)$ from Eq. (25) is shown in Fig. 2 in comparison with the exact result obtained by a numerical solution. Indeed, at $\sigma \gtrsim 3$ the results virtually coincide.

According to expansion (5), each decrement λ_ℓ defines the reference relaxation time

$$\tau_\ell = 2\tau_D/\lambda_\ell. \tag{26}$$

Thence from Eq. (25) we get

$$\tau_1 = 2\tau_D/\lambda_1 = \tau_{\mathrm{B}}\, G^2, \qquad \tau_{\mathrm{B}} \equiv 2\tau_D/\lambda_{\mathrm{B}}, \tag{27}$$

where τ_{B} denotes the asymptotic relaxation time obtained by Brown in Ref. 4. Substituting in Eq. (27) the explicit asymptotic series (12) for G, one gets

$$\tau_1 = \tau_D \frac{\sqrt{\pi}e^\sigma}{2\sigma^{3/2}} \left(1 + \frac{1}{\sigma} + \frac{7}{4\sigma^2} + \frac{9}{2\sigma^3} + \dots\right). \tag{28}$$

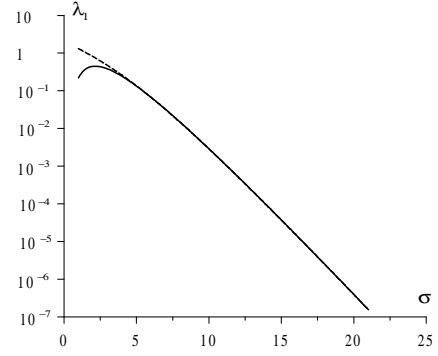### D. Asymptotic integral time

The decrements λ_ℓ or, equivalently, relaxation times τ_ℓ, being the characteristics of the eigenfunctions of the distribution function, are not observable if taken as separate quantities. However, in combination they are involved in a useful directly measurable quantity, the so-called integral relaxation time. In terms of correlation functions this characteristics is defined as

$$\tau_{\mathrm{int}} = \int_0^\infty \frac{\langle\, m(t)m(0)\,\rangle_0}{\langle\, m^2(0)\,\rangle_0}\, dt = \int_0^\infty \frac{\langle\, x(t)x(0)\,\rangle_0}{\langle\, x^2(0)\,\rangle_0}\, dt, \tag{29}$$

where the angular brackets stand for the statistical ensemble averaging over the equilibrium distribution (12). As follows from Eq. (29), the integral relaxation time equals the area under the normalized decay of magnetization.

The Green function of Eq. (2), i.e., the probability density of a state (x,t), provided the initial state is $(x_0, 0)$, writes

$$W(x,t;x_0,0) = \sum_{\ell=0}^\infty \psi_\ell(x)\, \varphi_\ell(x_0)\, e^{-\lambda_\ell t}. \tag{30}$$

Similarly to Eq. (7), we expand the eigenfunctions in Legendre polynomials as

$$\psi_\ell = \tfrac{1}{2} \sum_{k=1}^\infty (2k+1)\, b_k^{(\ell)} P_k(x), \qquad \varphi_\ell = \sum_{k=1}^\infty a_k^{(\ell)} P_k(x). \tag{31}$$

and introduce special notations for the first two functions

$$\psi_0 = \tfrac{1}{2} \sum_{k=0}^\infty (2k+1)\, S_k P_k(x), \tag{32}$$

$$\psi_1 = \tfrac{1}{2} \sum_{k=0}^\infty (2k+1)\, Q_k P_k(x).$$

The procedures to evaluate the coefficients S_k and Q_k and the explicit asymptotic forms for Q_1 and S_2 are given in Appendix A; note representation (11) for the equilibrium function ψ_0.

Due to Eq. (14), the coefficients in formulas (31) are related to each other by $b_k^{(\ell)} = \langle P_k P_{k'} \rangle_0\, a_{k'}^{(\ell)}$. In those terms one gets for the correlator in Eq. (14):

$$\langle\langle x(t)x(0) \rangle\rangle_0 = \int\int xx_0\, \psi_0\, W(x,t;x_0,0)\, dx\, dx_0 = \sum_{\ell=1} \left[b_1^{(\ell)} \right]^2 e^{-\lambda_\ell t/2\tau_D}, \qquad (33)$$

where the averaging over the current coordinate x is performed with the function W from Eq. (30) whereas that over the initial conditions—with the equilibrium function ψ_0. Substituting expression (33) in Eq. (29) one gets the integral time in the form

$$\tau_{\mathrm{int}} = \sum_{\ell=1}^{\infty} \tau_\ell \left[b_1^{(\ell)} \right]^2 \Big/ \sum_{\ell=1}^{\infty} \left[b_1^{(\ell)} \right]^2 = \sum_{\ell=1}^{\infty} \tau_\ell \left[b_1^{(\ell)} \right]^2 \Big/ \langle\, x^2\,\rangle_0 . \tag{34}$$

Unlike τ_1, which in principle cannot be evaluated[18] analytically at arbitrary σ, for τ_{int} an exact solution is possible for arbitrary values of the anisotropy parameter. Recently two ways were proposed to obtain quadrature formulas for τ_{int}. One method[19] implies a direct integration of the Fokker-Planck equation. Another method[20] involves solving three-term recurrence relations for the statistical moments of W. The emerging solution for τ_{int} can be expressed in a finite form in terms of hypergeometric (Kummer's) functions. Equivalence of both approaches was proven in Ref. 21.

In the present study, as mentioned, we are dealing in the high-barrier approximation. In this limiting case λ_1 is exponentially small, so that the term with $\ell = 1$ in the numerator in Eq. (34) is far greater than the others. With allowance for Eq. (32) it can be written as

$$\tau_{\mathrm{int}} = \tau_1 \left[b_1^{(1)} \right]^2 \Big/ \langle\, x^2\,\rangle_0 = \tau_1 Q_1^2 / \langle\, x^2\,\rangle_0. \tag{35}$$

The equilibrium moment calculated by definition writes

$$\langle\, x^2\,\rangle_0 = (1/2\sigma)\,(e^\sigma - 1) = 1/G - 1/2\sigma, \tag{36}$$

and for $\sigma \gg 1$, using formula (A5) of Appendix A we get

$$Q_1 \simeq 1/G. \tag{37}$$

Substitution of Eqs. (36) and (37) in (35) with allowance for relationships (12), (25) and (27) gives the asymptotic representation in the form

$$\begin{aligned}
\tau_{\mathrm{int}} &= \tau_{\mathrm{B}}\, \frac{2\sigma G}{(2\sigma - G)} \\
&= \tau_D \frac{\sqrt{\pi} e^\sigma}{2\sigma^{3/2}} \left(1 + \frac{1}{\sigma} + \frac{3}{2\sigma^2} + \frac{13}{4\sigma^3} + \dots \right).
\end{aligned} \tag{38}$$

As it is seen from formulas (28) and (38) written with the accuracy up to σ^{-3}, the asymptotic expressions for the interwell and integral times deviate beginning with the term $\propto \sigma^{-2}$. This contradicts the only known to us asymptotic expansion of τ_{int} given in Eq. (60) of Refs. 20 and repeated in Eq. (7.4.3.22) of the book [22]. The latter expression written with the accuracy $\propto \sigma^{-2}$, instead of turning into Eq. (38) coincides with the Brown's expression (28) for τ_1. Meanwhile, as it follows from formula (35), such a coincidence is impossible and therefore Eqs. (60) of Refs. 20 and (7.4.3.22) of Ref. 22 are misleading. The necessity to rectify this issue made us to begin the demonstration of our approach with the case of the integral relaxation time. Further on we consistently apply our procedure for description of the nonlinear (third- and fifth-harmonic) dynamic susceptibilities of a solid superparamagnetic dispersion.

III. PERTURBATIVE EXPANSIONS FOR THE DISTRIBUTION FUNCTION

A. Static probing field

To find the nonlinear susceptibilities, one has to take into account the changes that the probing field induces in the basic state of the system. In the limit $\sigma \gg 1$, which we deal in, the relaxation time τ_1 of the interwell mode ψ_1 is far greater than all the other relaxation times τ_k. This means that with respect to the intrawell modes the distribution function is in equilibrium. So it suffices to determine the effect of the probing field $\boldsymbol{H} = H\boldsymbol{h}$ just on ψ_0 and ψ_1. Assuming the energy function in the form

$$U + U_H = -Kv(\boldsymbol{e}\cdot\boldsymbol{n})^2 - IvH(\boldsymbol{e}\cdot\boldsymbol{h}), \tag{39}$$

[compare with Eq. (1)], and separating variables in Eq. (2), one arrives at the eigenfunction problem

$$\widehat{L} f_\beta = \xi \widehat{V} f_\beta, \tag{40}$$

where $\xi = IvH/kT$ and notation f_β refers to the distribution function modes that stem from ψ_0 or ψ_1 at $H \neq 0$, i.e., $\beta = 0$ or 1. In Eq. (40) operator $\widehat{L}$ is defined by Eq. (6) whilst $\widehat{V} = -\xi \widehat{\boldsymbol{J}}(\boldsymbol{e}\times\boldsymbol{h})$ is the operator caused by the energy term U_H in (Eq. 39). As in above, for the non-self-conjugated spectral problem (40) we introduce the family of conjugated functions g_β and set $f_\beta = g_\beta\psi_0$.

Following our approach, in the low-temperature limit ($\sigma \gg 1$) we *set to zero* the eigenvalues corresponding to

both f_0 and f_1; compare with Eqs. (17) and (18) for ψ_0 and ψ_1. Assuming the temperature-scaled magnetic field ξ to be small, we treat U_H as a perturbation Hamiltonian and expand the principal eigenfunctions as

$$f_0 = \sum_{n=0} \xi^n f_0^{(n)}, \qquad f_1 = \sum_{n=0} \xi^n f_1^{(n)}. \qquad (41)$$

Thence for the field-free ($H = 0$) case one has $f_0^{(0)} = \psi_0$ and $f_1^{(0)} = \psi_1$. The same kind of expansion is assumed for g_β with $g_0^{(0)} = 1$ and $g_1^{(0)} = \varphi_1$. Note also that in order to retain the normalizing condition we require that $f_\beta^{(n)}$ have zero averages.

Substituting expansion (41) in Eq. (40) and collecting the terms of the same order in ξ, we arrive at the recurrence relation

$$\widehat{L} f_\beta^{(n)} = \widehat{V} f_\beta^{(n-1)}, \qquad (42)$$

that for the particular cases $\beta = 0$ and 1 with the aid of the identity $\boldsymbol{e} \times \boldsymbol{h} = \widehat{\boldsymbol{J}}(\boldsymbol{e} \cdot \boldsymbol{h})$ takes the formes

$$\widehat{\boldsymbol{J}}\psi_0 \widehat{\boldsymbol{J}} g_0^{(n)} = \widehat{\boldsymbol{J}}\psi_0 g_0^{(n-1)} \widehat{\boldsymbol{J}}(\boldsymbol{e} \cdot \boldsymbol{h}), \qquad (43)$$
$$\widehat{\boldsymbol{J}}\psi_0 \widehat{\boldsymbol{J}} g_1^{(n)} = \widehat{\boldsymbol{J}}\psi_0 g_1^{(n-1)} \widehat{\boldsymbol{J}}(\boldsymbol{e} \cdot \boldsymbol{h}),$$

respectively. Set (43) solves easily for g_0 since $g_0^{(0)} = \varphi_0 = 1$. Starting with $n = 0$, one gets sequentially

$$
\begin{aligned}
g_0^{(1)} &= (\boldsymbol{e} \cdot \boldsymbol{h}), &(44)\\
g_0^{(2)} &= \tfrac{1}{2}\left[(\boldsymbol{eh})^2 - \langle (\boldsymbol{e} \cdot \boldsymbol{h})^2 \rangle_0\right], \\
g_0^{(3)} &= \tfrac{1}{6}(\boldsymbol{e} \cdot \boldsymbol{h})^3 - \tfrac{1}{2}(\boldsymbol{e} \cdot \boldsymbol{h})\langle (\boldsymbol{e} \cdot \boldsymbol{h})^2 \rangle_0, \\
g_0^{(4)} &= \tfrac{1}{24}\left[(\boldsymbol{e} \cdot \boldsymbol{h})^4 - \langle (\boldsymbol{e} \cdot \boldsymbol{h})^4 \rangle_0\right] - \tfrac{1}{4}\left[(\boldsymbol{e} \cdot \boldsymbol{h})^2\langle (\boldsymbol{e} \cdot \boldsymbol{h})^2 \rangle_0 - \langle (\boldsymbol{e} \cdot \boldsymbol{h})^2 \rangle_0^2\right], \\
g_0^{(5)} &= \tfrac{1}{120}(\boldsymbol{e} \cdot \boldsymbol{h})^5 - \tfrac{1}{12}(\boldsymbol{e} \cdot \boldsymbol{h})^3\langle (\boldsymbol{e} \cdot \boldsymbol{h})^2 \rangle_0 - \tfrac{1}{24}(\boldsymbol{e} \cdot \boldsymbol{h})\left[\langle (\boldsymbol{e} \cdot \boldsymbol{h})^4 \rangle_0 - 6\langle (\boldsymbol{e} \cdot \boldsymbol{h})^2 \rangle_0^2\right].
\end{aligned}
$$

All the obtained functions are constructed in such a way that the corresponding $f_\beta^{(n)}$ satisfy the above-mentioned zero average requirement. We remark also that there is no problem to continue the calculational procedure to any order.

Evaluation of g_1 is done in two steps. At the first one, we set $g_1^{(0)}$ equal to the antisymmetric step-wise function (23) and its derivative equal zero. After that from the second of Eqs. (43) we can express $g_1^{(k)}$ in closed form. Taken up to the fourth order these "zero-derivative" solutions write

$$
\begin{aligned}
g_1^{(1)} &= \varphi_1 (\boldsymbol{e} \cdot \boldsymbol{h}) - \langle \varphi_1(\boldsymbol{e} \cdot \boldsymbol{h}) \rangle_0, &(45)\\
g_1^{(2)} &= \tfrac{1}{2}\varphi_1(\boldsymbol{e} \cdot \boldsymbol{h})^2 - (\boldsymbol{e} \cdot \boldsymbol{h})\langle \varphi_1(\boldsymbol{e} \cdot \boldsymbol{h}) \rangle_0, \\
g_1^{(3)} &= \tfrac{1}{6}\left[\varphi_1 (\boldsymbol{e} \cdot \boldsymbol{h})^3 - \langle \varphi_1(\boldsymbol{e} \cdot \boldsymbol{h})^3 \rangle_0\right] - \tfrac{1}{2}\langle \varphi_1(\boldsymbol{e} \cdot \boldsymbol{h}) \rangle_0\left[(\boldsymbol{e} \cdot \boldsymbol{h})^2 - \langle (\boldsymbol{e} \cdot \boldsymbol{h})^2 \rangle_0\right], \\
g_1^{(4)} &= \tfrac{1}{24}\varphi_1 (\boldsymbol{e} \cdot \boldsymbol{h})^4 - \tfrac{1}{6}\langle \varphi_1 (\boldsymbol{e} \cdot \boldsymbol{h}) \rangle_0\left[(\boldsymbol{e} \cdot \boldsymbol{h})^3 - 3(\boldsymbol{e} \cdot \boldsymbol{h})\langle (\boldsymbol{e} \cdot \boldsymbol{h})^2 \rangle_0\right] \\
&\qquad\qquad - \tfrac{1}{6}(\boldsymbol{e} \cdot \boldsymbol{h})\langle \varphi_1 (\boldsymbol{e} \cdot \boldsymbol{h})^3 \rangle_0.
\end{aligned}
$$

Note the alternating parity in $\boldsymbol{e}$ with the term order growth in both Eqs. (44) and (45).

It is instructive to compare the approximate expressions (45) with the numerical results obtained without simplification of $g_1^{(0)}$. To be specific, we consider the case when probing field is applied along the particle easy axis $\boldsymbol{n}$. Then Eqs. (43) become one-dimensional and the second of them writes

$$\frac{dg_1^{(n)}}{dx} = g_1^{(n-1)}. \qquad (46)$$

Its "zero-derivative" solutions up to the second order follow from the first two lines of Eqs. (45):

$$g_1^{(1)} = \varphi_1 x - \langle \varphi_1 x \rangle_0, \qquad g_1^{(2)} = \tfrac{1}{2}\varphi_1 x^2 - x\langle \varphi_1 x \rangle_0. \qquad (47)$$

In Figs. 3 and 4 these functions are compared to the numerical solutions of Eq. (46). For our calculation, the most important is the behavior of those functions near $x = \pm 1$ since these regions yield the main contribution when integrated with the weight function ψ_0. As one can see from the figures, the "zero-derivative" solution $g_1^{(1)}$ agrees well with the exact one, whilst $g_1^{(2)}$ deviates significantly. This discrepancy is due to the change of the barrier height that occurs in the second order with respect to the probing field amplitude, and manifests itself in all the even orders of the perturbation expansion. Correction of solution (47) makes the second step of our procedure. For that we integrate Eq. (46) two times by parts and substitute there the "zero-derivative" form of
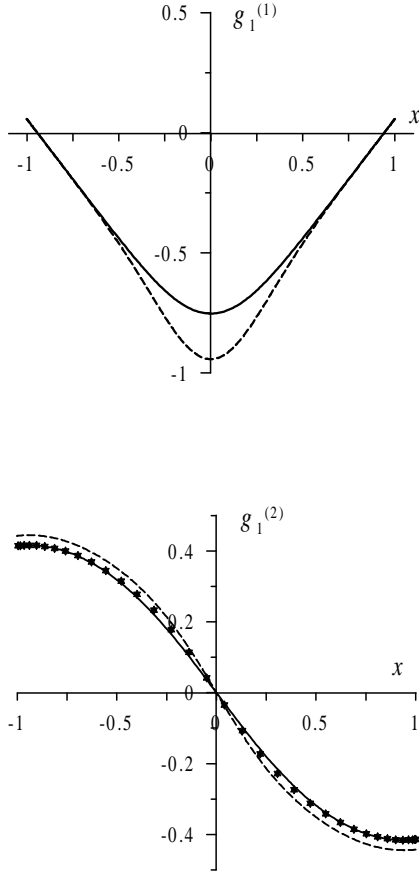
FIG. 4: Function $g_1^{(2)}$ found numerically (solid) and evaluated in the "zero-derivative" approximation (dashed). Asterisks show a corrected calculation with allowance for the coefficient D_2, see Eq. (49).

$g_1^{(1)}$ from Eq. (47):

$$g_1^{(2)} = \frac{1}{2} x^2 \varphi_1 - x\langle x\varphi_1 \rangle + \frac{1}{2}\int x^2 \frac{d\varphi_1}{dx} dx, \qquad (48)$$

Thus one finds that the corrected $g_1^{(2)}$ differs from this of Eq. (47) by adding a step-wise [alike that of Eq. (23)]

term

$$g_1^{(2)} = \frac{1}{2} x^2 \varphi_1 - x\langle x\varphi_1 \rangle + D_2\varphi_1, \qquad (49)$$

with the amplitude

$$D_2 = \frac{1}{2}\int_0^1 x^2 \frac{d\varphi_1}{dx} dx. \qquad (50)$$

We remark that the results of evaluation of the integrals $I_{2k} = \int_0^1 x^{2k} (d\varphi_1/dx)\, dx$ can be arranged in the table

k	0	1	2
I_{2k}	1	$1-G^{-1}$	$1-(1+1/2\sigma)\,G^{-1}$
(51)

so that Eq. (50) gives

$$D_2 = \frac{1}{2} I_{2k} = \frac{G-1}{2G} = \frac{1}{4\sigma}+\frac{1}{4\sigma^2}+\frac{5}{8\sigma^3}+\frac{37}{16\sigma^4}+\dots \quad (52)$$

Function $g_1^{(2)}$ corrected in such a way is shown in Fig. 4 by asterisks. It is seen that the corrected dependence with a fairly good accuracy follows the the numerically obtained curve.

In a similar way one can prove that the corrected function $g_1^{(4)}$ has the form

$$g_1^{(4)} = \frac{1}{24}\varphi_1 x^4 - \frac{1}{6}\left[\langle \varphi_1 x \rangle_0 x^3 - 3x\langle x^2 \rangle_0\right] \qquad (53)$$
$$-\frac{1}{6}x\langle \varphi_1 x^3 \rangle_0 + D_2 g_1^{(2)} + D_4\varphi_1,$$

where the corrected function $g_1^{(2)}$ given by Eq. (49) is used and

$$D_4 = \frac{1}{24} I_4 - D_2^2 = -\frac{10\sigma G^2 - 22\sigma G + G + 12\sigma}{48\sigma G^2} \quad (54)$$
$$= -\frac{1}{32\sigma^2} - \frac{1}{16\sigma^3} - \frac{5}{32\sigma^4} - \frac{29}{64\sigma^5} + \dots$$

In the general case, when the direction of the probing field does not coincide with the particle anisotropy axis, the corrected functions $g_1^{(n)}$ still can be written as

$$g_1^{(2)} = \frac{1}{2}\varphi_1 (\boldsymbol{e}\cdot\boldsymbol{h})^2 - (\boldsymbol{e}\cdot\boldsymbol{h})\langle \varphi_1(\boldsymbol{e}\cdot\boldsymbol{h})\rangle_0 + D_2\varphi_1,$$
$$g_1^{(3)} = \frac{1}{6}\left[\varphi_1 (\boldsymbol{e}\cdot\boldsymbol{h})^3 - \langle \varphi_1(\boldsymbol{e}\cdot\boldsymbol{h})^3 \rangle_0\right] - \frac{1}{2}\langle\varphi_1(\boldsymbol{e}\cdot\boldsymbol{h})\rangle_0 \left[(\boldsymbol{e}\cdot\boldsymbol{h})^2 - \langle (\boldsymbol{e}\cdot\boldsymbol{h})^2 \rangle_0\right] + D_2 g_1^{(1)},$$
$$g_1^{(4)} = \frac{1}{24}\varphi_1 (\boldsymbol{e}\cdot\boldsymbol{h})^4 - \frac{1}{6}\langle\varphi_1(\boldsymbol{e}\cdot\boldsymbol{h})\rangle_0 \left[(\boldsymbol{e}\cdot\boldsymbol{h})^3 - 3(\boldsymbol{e}\cdot\boldsymbol{h})\langle (\boldsymbol{e}\cdot\boldsymbol{h})^2 \rangle_0\right]$$
$$-\frac{1}{6}(\boldsymbol{e}\cdot\boldsymbol{h})\langle \varphi_1(\boldsymbol{e}\cdot\boldsymbol{h})^3 \rangle_0 + D_2 g_1^{(2)} + D_4\varphi_1. \qquad (55)$$

But since Eqs. (43) cannot be reduced to a form like Eq. (46), the correcting coefficients D_2 and D_4 cannot be presented in a closed form. In this case the corrected

solutions taking into account the behavior of function φ_1 around zero are built up as power series near $x = 0$; such a procedure for the coefficients D_2 and D_4 is described

in Appendix B.

B. Dynamic probing field

To obtain the dynamic susceptibilities, one has to find the distribution function W in the oscillating probing field $\xi \exp(i\omega t)$. For this situation the kinetic equation (2) takes the form

$$\left(2\tau_D \frac{\partial}{\partial t} + \widehat{L}\right) W(t) = \xi \widehat{V} e^{i\omega t} W(t), \qquad (56)$$

where the operators $\widehat{L}$ and $\widehat{V}$ have been introduced in above. Assuming that the exciting field amplitude is not too high, we expand the steady-state oscillatory solution of Eq. (56) in a power series with respect to ξ:

$$W(t) = \sum_{n=0} \xi^n W^{(n)} e^{in\omega t}. \qquad (57)$$

Note that, mathematically, representation (57) is not complete. Indeed, in a general case the exact amplitude of the $n\omega$-mode must contain, along with the contribution $\sim \xi^n$, an infinite set of terms $\sim \xi^{n+2}$, ξ^{n+4}, etc. However, in a weak field limit $\xi < 1$ the terms with higher powers are of minor importance so that the main contribution to the magnetization response signal filtered at the frequency $n\omega$ is proportional to ξ^n.

Substituting Eq. (57) in (56) we arrive at the recurrence set

$$\left(2in\omega\tau_D + \widehat{L}\right) W^{(n)} = \widehat{V} W^{(n-1)}, \qquad (58)$$

that we solve sequentially starting from $n = 1$. At the first step the function in the right-hand side corresponds to the equilibrium case ($\xi = 0$). Therefore, $W^{(0)} = \psi_0$, where the latter function is defined by Eq. (11) and is frequency-independent. Combining Eq. (42) written down for $\beta = 0$ and $n = 1$ and Eq. (58), we eliminate the operator $\widehat{V}$ and get

$$\left(2i\omega\tau_D + \widehat{L}\right) W^{(1)} = \widehat{L} f_0^{(1)}. \qquad (59)$$

Now we expand the functions subjected to operator $\widehat{L}$ with respect to the set $\{\psi_k\}$ of its eigenfunctions, see Eq. (6):

$$W^{(1)} = \sum c_j^{(1)}(\omega)\psi_j \qquad f_0^{(1)} = \sum \left(\varphi_j \big| f_0^{(1)}\right)\psi_j; \qquad (60)$$

here $(\varphi|f)$ denotes functional scalar multiplication, i.e., the integral of the product φf over all the orientations of $\boldsymbol{e}$. Substitution of Eq. (60) in (59), multiplication of it from the left by φ_k and integration, render the expansion coefficient as

$$c_k^{(1)}(\omega) = \left(\varphi_k \big| f_0^{(1)}\right) [1 + i\omega\tau_k]^{-1}, \qquad (61)$$

where the reference relaxation times are defined by Eq. (26).

In the low-frequency limit only $\omega\tau_1$ is set to be nonzero whilst all the higher modes are taken at equilibrium ($\omega\tau_k = 0$). Thence, when constructing $W^{(1)}$ via Eq. (60), by adding and subtracting a term with $c_1^{(1)}(0)$, one can present the first-order solution in the form

$$W^{(1)} = f_0^{(1)} - \frac{i\omega\tau_1}{1 + i\omega\tau_1} \left(\varphi_1 \big| f_0^{(1)}\right)\psi_1, \qquad (62)$$

where $f_0^{(1)}$, as seen from Eq. (59), is the equilibrium solution for the same value of the field amplitude ξ. We remind that the functions without upper index belong to the fundamental set defined by Eqs. (6) whereas those with an upper index are evaluated in the framework of the perturbation scheme described in Sec. III A.

In the next order in ξ the function $W^{(1)}$ is substituted in the right-hand side of Eq. (58) and through a procedure alike to that leading to Eqs. (59)–(61), the function $W^{(2)}$ is found. We carry on this cycle up to $k = 5$. The results write

$$W^{(2)} = f_0^{(2)} - \frac{i\omega\tau_1}{1 + i\omega\tau_1} \left(\varphi_1 \big| f_0^{(1)}\right) f_1^{(1)}, \qquad (63)$$

$$
\begin{aligned}
W^{(3)} = f_0^{(3)} &+ \left[\left(\varphi_1 \big| f_0^{(1)}\right)\left(\varphi_1 \big| f_1^{(2)}\right) - \left(\varphi_1 \big| f_0^{(3)}\right)\right] f_1^{(0)} - \left(\varphi_1 \big| f_0^{(1)}\right) f_1^{(2)} \\
&+ \frac{1}{1 + i\omega\tau_1}\left[\left(\varphi_1 \big| f_0^{(1)}\right) f_1^{(2)} - \tfrac{3}{2}\left(\varphi_1 \big| f_0^{(1)}\right)\left(\varphi_1 \big| f_1^{(2)}\right) f_1^{(0)}\right] \\
&+ \frac{1}{1 + 3i\omega\tau_1}\left[\left(\varphi_1 \big| f_0^{(3)}\right) + \tfrac{1}{2}\left(\varphi_1 \big| f_0^{(1)}\right)\left(\varphi_1 \big| f_1^{(2)}\right)\right] f_1^{(0)},
\end{aligned} \qquad (64)
$$

$$W^{(4)} = f_0^{(4)} + \left[\left(\varphi_1 \middle| f_0^{(1)} \right) \left(\varphi_1 \middle| f_1^{(2)} \right) - \left(\varphi_1 \middle| f_0^{(3)} \right) \right] f_1^{(1)} - \left(\varphi_1 \middle| f_0^{(1)} \right) f_1^{(3)}$$
$$+ \frac{1}{1 + i\omega\tau_1} \left[\left(\varphi_1 \middle| f_0^{(1)} \right) f_1^{(3)} - \tfrac{3}{2} \left(\varphi_1 \middle| f_0^{(1)} \right) \left(\varphi_1 \middle| f_1^{(2)} \right) f_1^{(1)} \right]$$
$$+ \frac{1}{1 + 3i\omega\tau_1} \left[\left(\varphi_1 \middle| f_0^{(3)} \right) + \tfrac{1}{2} \left(\varphi_1 \middle| f_0^{(1)} \right) \left(\varphi_1 \middle| f_1^{(2)} \right) \right] f_1^{(1)}, \tag{65}$$

$$\begin{aligned} W^{(5)} =\ & f_0^{(5)} - \left(\varphi_1 \middle| f_0^{(5)} \right) f_1^{(0)} + \left(\varphi_1 \middle| f_0^{(1)} \right) \left[\left(\varphi_1 \middle| f_1^{(4)} \right) f_1^{(0)} - f_1^{(4)} \right] \\ & + \left[\left(\varphi_1 \middle| f_0^{(1)} \right) \left(\varphi_1 \middle| f_1^{(2)} \right) - \left(\varphi_1 \middle| f_0^{(3)} \right) \right] \left[f_1^{(2)} - \left(\varphi_1 \middle| f_1^{(2)} \right) f_1^{(0)} \right] \\ & + \frac{1}{1 + i\omega\tau_1} \left(\varphi_1 \middle| f_0^{(1)} \right) \left\{ f_1^{(4)} - \tfrac{3}{2} \left(\varphi_1 \middle| f_1^{(2)} \right) f_1^{(2)} + \left[\tfrac{15}{8} \left(\varphi_1 \middle| f_1^{(2)} \right)^2 - \tfrac{5}{4} \left(\varphi_1 \middle| f_1^{(4)} \right) \right] f_1^{(0)} \right\} \\ & + \frac{1}{1 + 3i\omega\tau_1} \left[\left(\varphi_1 \middle| f_0^{(3)} \right) + \tfrac{1}{2} \left(\varphi_1 \middle| f_0^{(1)} \right) \left(\varphi_1 \middle| f_1^{(2)} \right) \right] \left[f_1^{(2)} - \tfrac{5}{2} \left(\varphi_1 \middle| f_1^{(2)} \right) f_1^{(0)} \right] \\ & + \frac{1}{1 + 5i\omega\tau_1} \left[\left(\varphi_1 \middle| f_0^{(5)} \right) + \tfrac{1}{4} \left(\varphi_1 \middle| f_0^{(1)} \right) \left(\varphi_1 \middle| f_1^{(4)} \right) + \tfrac{3}{8} \left(\varphi_1 \middle| f_0^{(1)} \right) \left(\varphi_1 \middle| f_1^{(2)} \right)^2 \right. \\ & \hspace{6cm} \left. + \tfrac{3}{2} \left(\varphi_1 \middle| f_0^{(3)} \right) \left(\varphi_1 \middle| f_1^{(2)} \right) \right] f_1^{(0)}. \end{aligned} \tag{66}$$

We remark an important feature of Eqs. (63)–(66): they do not contain dispersion factors of even orders. This ensures that the frequency dependence of the full distribution function W incorporates only dispersion factors with odd multiples of the basic frequency. Qualitatively, this is the result of absence of the interwell mode for the statistical moments of even orders. Technically, it is due to vanishing of the products $\left(\varphi_1 \middle| f_k^{(\ell)} \right)$ entering Eqs. (62)–(66) if the sum $k + \ell$ is even. This rule follows immediately from combination of the oddity of φ_1, see Sec. II, with the parity properties of the functions $f_k^{(\ell)}$ introduced in Sec. III A.

For actual calculations one needs the values of the scalar products entering Eqs. (62)–(66). In Appendix C we obtain their representations in terms of the moments Q_k and S_k of the functions ψ_0 and ψ_1, respectively. The procedures of asymptotic expansion of Q_k and S_k are given in Appendix A.

IV. DYNAMIC SUSCEPTIBILITIES

The set of magnetic susceptibilities of an assembly of non-interacting particles with the number density c is defined by the relation

$$M = \chi^{(1)} H + \chi^{(3)} H^3 + \chi^{(5)} H^5 + \dots \tag{67}$$

that describes the magnetization of the system in the direction of the probing field $\boldsymbol{H} = H\boldsymbol{h}$. Therefore, of all the components of the corresponding susceptibility tensors, we retain the combinations that determine the response

in the direction of the probing field. With representation (57) for the distribution function, this magnetization component takes the form

$$\begin{aligned} M &= cIv\langle (\boldsymbol{e} \cdot \boldsymbol{h}) \rangle \\ &= c \sum_{n=1} H^n \frac{I^{n+1} v^{n+1}}{(kT)^n} e^{in\omega t} \int (\boldsymbol{e} \cdot \boldsymbol{h}) W^{(n)} \, d\boldsymbol{e}, \end{aligned} \tag{68}$$

and the susceptibilities can be found by a direct comparison with Eq. (67). In other words, the set of $\chi^{(n)}$ is expressed through the perturbation functions $W^{(n)}$ found in the preceding section. Therefore, evaluation of $\chi^{(n)}$ becomes, although tedious, but simple procedure. Remarkably, the final expressions come out rather compact.

A. Linear susceptibility

The resulting expression can be presented in the form

$$\chi_\omega^{(1)} = \chi_0^{(1)} \left(B_0^{(1)} + \frac{B_1^{(1)}}{1 + i\omega\tau_1} \right), \qquad \chi_0^{(1)} = \frac{cI^2 v^2}{3kT}, \tag{69}$$

which follows from substituting Eq. (62) in (68). Each of the two frequency-independent coefficients $B^{(1)}$, being the result of statistical averaging over the orientational variable $\boldsymbol{e}$, see Appendix C, expands into a series of Legendre polynomials with respect to β, the angle between the direction $\boldsymbol{h}$ of the probing field and the particle easy

axis $\boldsymbol{n}$. This can be written as

$$
\begin{cases}
B_0^{(1)} = b_{00}^{(1)} + b_{02}^{(1)} P_2(\cos\beta), \\
B_1^{(1)} = b_{10}^{(1)} + b_{12}^{(1)} P_2(\cos\beta),
\end{cases}
\tag{70}
$$

$$
\begin{pmatrix} b_{00}^{(1)} & b_{02}^{(1)} \\ b_{10}^{(1)} & b_{12}^{(1)} \end{pmatrix} = \begin{pmatrix} 1 - Q_1^2 & 2S_2 - 2Q_1^2 \\ Q_1^2 & 2Q_1^2 \end{pmatrix}.
$$

Definitions of functions Q_1 and S_2 and their explicit asymptotic representations are given in Appendix A. The asymptotic series for the coefficients $b_{\alpha\beta}^{(1)}$ derived on the base of expansion (12) and Eq. (37) are

$$
b_{02}^{(1)} = -\frac{1}{\sigma} + \frac{1}{4\sigma^3} + \frac{13}{8\sigma^4} + \frac{165}{16\sigma^5} + \frac{2273}{32\sigma^6} + \frac{34577}{64\sigma^7} + \frac{581133}{128\sigma^8} + \dots
\tag{71}
$$

$$
b_{10}^{(1)} = 1 - \frac{1}{\sigma} - \frac{3}{4\sigma^2} - \frac{2}{\sigma^3} - \frac{31}{4\sigma^4} - \frac{153}{4\sigma^5} - \frac{3629}{16\sigma^6} - \frac{1564}{\sigma^7} - \frac{785931}{64\sigma^8} + \dots
$$

The other components, namely, $b_{00}^{(1)}$ and $b_{12}^{(1)}$, may be constructed straightforwardly using their relations with the given ones, see Eqs. (70). For a random system, that is for an assembly of non-interacting particles with a chaotic distribution of the anisotropy axes, the average of any Legendre polynomial is zero, so that $\overline{B^{(1)}}_k = b_{k0}^{(1)}$, and the linear dynamic susceptibility reduces to

$$
\overline{\chi^{(1)}}_\omega = \chi_0^{(1)} \frac{1 + i\omega\tau_1 b_{00}}{1 + i\omega\tau_1},
\tag{72}
$$

that is the asymptotic representation of the full expression given by formula (39) of Ref. [6].

B. Cubic susceptibility

As follows from definitions (67) and (68), the third-order susceptibility is defined through the response at the triple frequency that at weak H scales as H^3. Performing calculations along the same scheme as for $\chi^{(1)}$, one arrives at the sum-of-relaxators representation

$$
\chi_{3\omega}^{(3)} = \frac{1}{4} \chi_0^{(3)} \left(B_0^{(3)} + \frac{B_1^{(3)}}{1 + i\omega\tau_1} + \frac{B_3^{(3)}}{1 + 3i\omega\tau_1} \right),
\tag{73}
$$

$$
\chi_0^{(3)} = \frac{cI^4v^4}{(kT)^3},
$$

where the coefficients expand as

$$
B_k^{(3)} = b_{k0}^{(3)} + b_{k2}^{(3)} P_2(\cos\beta) + b_{k4}^{(3)} P_4(\cos\beta), \quad k = 0, 1, 3 \dots
\tag{74}
$$

up to the fourth Legendre polynomial in $\cos\beta$.

The explicit expansions for the amplitudes $b_{\alpha\beta}^{(3)}$ are

$$
\begin{aligned}
b_{00}^{(3)} &= \frac{1}{30\sigma^3} + \frac{47}{240\sigma^4} + \frac{49}{40\sigma^5} + \frac{815}{96\sigma^6} + \frac{7837}{120\sigma^7} + \frac{355391}{640\sigma^8} + \dots \\[4pt]
b_{02}^{(3)} &= \frac{1}{42\sigma^3} + \frac{2}{21\sigma^4} + \frac{4}{7\sigma^5} + \frac{1385}{336\sigma^6} + \frac{11231}{336\sigma^7} + \frac{19083}{64\sigma^8} + \dots \\[4pt]
b_{04}^{(3)} &= -\frac{2}{35\sigma^3} - \frac{8}{35\sigma^4} - \frac{41}{35\sigma^5} - \frac{50}{7\sigma^6} - \frac{1756}{35\sigma^7} - \frac{63749}{160\sigma^8} + \dots \\[4pt]
b_{10}^{(3)} &= \frac{1}{15} - \frac{1}{6\sigma} - \frac{23}{240\sigma^2} - \frac{61}{192\sigma^3} - \frac{1357}{960\sigma^4} - \frac{235447}{30720\sigma^5} - \frac{11962691}{245760\sigma^6} - \frac{694849241}{1966080\sigma^7} - \frac{15133953221}{5242880\sigma^8} + \dots \\[4pt]
b_{12}^{(3)} &= \frac{13}{84} - \frac{65}{168\sigma} - \frac{25}{168\sigma^2} - \frac{863}{1344\sigma^3} - \frac{3931}{1344\sigma^4} - \frac{698911}{43008\sigma^5} - \frac{35309123}{344064\sigma^6} - \frac{2061480665}{2752512\sigma^7} - \frac{45071465669}{7340032\sigma^8} + \dots \\[4pt]
b_{14}^{(3)} &= \frac{1}{35} - \frac{1}{14\sigma} + \frac{2}{35\sigma^2} - \frac{1}{112\sigma^3} - \frac{73}{560\sigma^4} - \frac{17033}{17920\sigma^5} - \frac{1007549}{143360\sigma^6} - \frac{64390439}{1146880\sigma^7} - \frac{4493994417}{9175040\sigma^8} + \dots \\[4pt]
b_{30}^{(3)} &= -\frac{2}{15} + \frac{3}{10\sigma} + \frac{1}{16\sigma^2} + \frac{337}{960\sigma^3} + \frac{499}{320\sigma^4} + \frac{85309}{10240\sigma^5} + \frac{2563751}{49152\sigma^6} + \frac{245269747}{655360\sigma^7} + \frac{47628510799}{15728640\sigma^8} + \dots \\[4pt]
b_{32}^{(3)} &= -\frac{29}{84} + \frac{43}{56\sigma} + \frac{11}{56\sigma^2} + \frac{1279}{1344\sigma^3} + \frac{1881}{448\sigma^4} + \frac{320765}{14336\sigma^5} + \frac{48133699}{34406\sigma^6} + \frac{920146163}{91750\sigma^7} + \frac{178560431695}{22020096\sigma^8} + \dots \\[4pt]
b_{34}^{(3)} &= -\frac{11}{105} + \frac{47}{210\sigma} + \frac{2}{21\sigma^2} + \frac{559}{1680\sigma^3} + \frac{2419}{1680\sigma^4} + \frac{409499}{53760\sigma^5} + \frac{4080395}{86016\sigma^6} + \frac{1166954357}{3440640\sigma^7} + \frac{75334335763}{27525120\sigma^8} + \dots
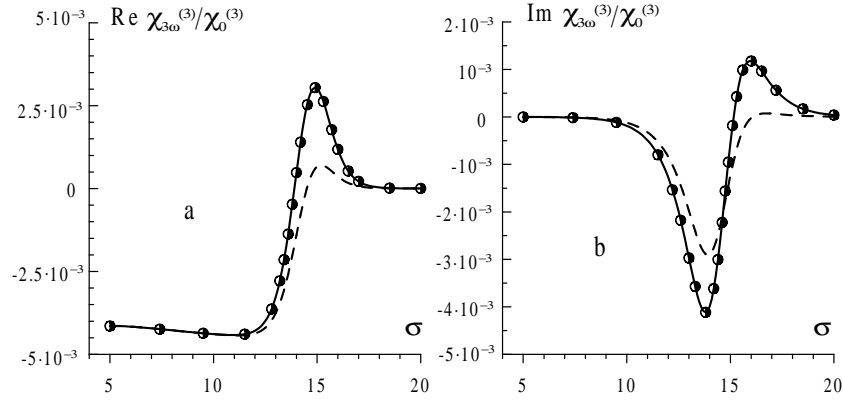\end{aligned}
\tag{75}
$$

FIG. 5: Real (a) and imaginary (b) components of the cubic susceptibility of a superparamagnetic assembly with coherently aligned easy axes; the direction of the probing field is tilted with respect to the alignment axis at $\cos\beta = 0.5$; the dimensionless frequency is $\omega\tau_0 = 10^{-6}$. Solid lines show the proposed asymptotic formulas taken with the accuracy σ^{-3}, circles present the result of numerically-exact evaluation, dashed lines correspond to the "zero-derivative" approximation (45). The discrepancy of the curves is commented in the text after Eq. (B12).

For a random system, the averages of Legendre polynomials drop out and $\overline{B_k^{(3)}} = b_{k0}^{(3)}$. With respect to formalism constructed in Ref. [6], the above expressions yield the asymptotic representations for formulas (42) and (43) there.

C.   Fifth-order susceptibility

The susceptibility of the fifth order writes in an expectable way as a sum of three relaxators:

$$\chi_{5\omega}^{(5)} = \frac{1}{16}\chi_0^{(5)}\left(B_0^{(5)} + \frac{B_1^{(5)}}{1+i\omega\tau} + \frac{B_3^{(5)}}{1+3i\omega\tau} + \frac{B_5^{(5)}}{1+5i\omega\tau}\right), \qquad \chi_0^{(5)} = \frac{cI^6v^6}{(kT)^5}, \tag{76}$$

with the coefficients

$$B_k^{(5)} = b_{k0}^{(5)} + b_{k2}^{(5)}P_2(\cos\beta) + b_{k4}^{(5)}P_4(\cos\beta) + b_{k6}^{(5)}P_6(\cos\beta) \qquad k = 0, 1, 3, 5. \tag{77}$$

The explicit asymptotic series are

$$b_{00}^{(5)} = \frac{1}{80\sigma^5} + \frac{367}{2240\sigma^6} + \frac{123}{70\sigma^7} + \frac{41233}{2240\sigma^8} + \dots$$

$$b_{10}^{(5)} = \frac{1}{96} - \frac{19}{420\sigma} + \frac{1}{120\sigma^2} - \frac{65}{1792\sigma^3} - \frac{79}{336\sigma^4} - \frac{85913}{57344\sigma^5} - \frac{72636131}{6881280\sigma^6} - \frac{4543038053}{55050240\sigma^7} - \frac{14938598691}{20971520\sigma^8} + \dots$$

$$b_{30}^{(5)} = -\frac{47}{560} + \frac{11}{35\sigma} - \frac{29}{280\sigma^2} + \frac{437}{1920\sigma^3} + \frac{5473}{4480\sigma^4} + \frac{1046209}{143360\sigma^5} + \frac{169435283}{3440640\sigma^6} + \frac{684614895}{1835008\sigma^7} + \frac{230861266333}{73400320\sigma^8} + \dots$$

$$b_{50}^{(5)} = \frac{311}{3360} - \frac{137}{420\sigma} + \frac{13}{105\sigma^2} - \frac{5911}{26880\sigma^3} - \frac{2141}{1920\sigma^4} - \frac{1874309}{286720\sigma^5} - \frac{299470403}{6881280\sigma^6} - \frac{17964831133}{55050240\sigma^7} - \frac{400677748549}{146800640\sigma^8} + \dots$$

$$b_{02}^{(5)} = \frac{1}{112\sigma^5} + \frac{3}{28\sigma^6} + \frac{507}{448\sigma^7} + \frac{5377}{448\sigma^8} + \dots$$

$$b_{12}^{(5)} = \frac{13}{504} - \frac{19}{168\sigma} + \frac{23}{672\sigma^2} + \frac{737}{8064\sigma^3} - \frac{2959}{5376\sigma^4} - \frac{99733}{28672\sigma^5} - \frac{50499149}{2064384\sigma^6} - \frac{350973527}{1835008\sigma^7} - \frac{72765921299}{44040192\sigma^8} + \dots$$

$$b_{32}^{(5)} = -\frac{5}{21} + \frac{149}{168\sigma} - \frac{193}{672\sigma^2} + \frac{5245}{8064\sigma^3} + \frac{18677}{5376\sigma^4} + \frac{1785635}{86016\sigma^5} + \frac{289305193}{2064384\sigma^6} + \frac{5846947361}{5505024\sigma^7} + \frac{394448762615}{44040192\sigma^8} + \dots$$

$$b_{52}^{(5)} = \frac{139}{504} - \frac{27}{28\sigma} + \frac{109}{336\sigma^2} - \frac{1343}{2016\sigma^3} - \frac{9203}{2688\sigma^4} - \frac{431321}{21504\sigma^5} - \frac{9839105}{73728\sigma^6} - \frac{196654913}{196608\sigma^7} - \frac{30690812563}{3670016\sigma^8} + \dots$$

$$b_{04}^{(5)} = -\frac{3}{140\sigma^5} - \frac{1563}{6160\sigma^6} - \frac{7767}{3080\sigma^7} - \frac{613353}{24640\sigma^8} + \dots$$

$$b_{14}^{(5)} = \frac{15}{2464} - \frac{183}{6160\sigma} + \frac{713}{24640\sigma^2} - \frac{433}{19712\sigma^3} - \frac{409}{4928\sigma^4} - \frac{319665}{630784\sigma^5} - \frac{8222083}{2293760\sigma^6} - \frac{5744848239}{201850880\sigma^7} - \frac{403943151013}{1614807040\sigma^8} + \dots$$

$$b_{34}^{(5)} = -\frac{29}{280} + \frac{293}{770\sigma} - \frac{47}{385\sigma^2} + \frac{7081}{24640\sigma^3} + \frac{74647}{49280\sigma^4} + \frac{7137293}{788480\sigma^5} + \frac{385804437}{6307840\sigma^6} + \frac{4682760003}{10092544\sigma^7} + \frac{1580817298041}{403701760\sigma^8} + \dots$$

$$b_{54}^{(5)} = \frac{1713}{12320} - \frac{2929}{6160\sigma} + \frac{2551}{24640\sigma^2} - \frac{34863}{98560\sigma^3} - \frac{92061}{49280\sigma^4} - \frac{34432191}{3153920\sigma^5} - \frac{23756287}{327680\sigma^6} - \frac{15647080587}{28835840\sigma^7} - \frac{7317549380671}{1614807040\sigma^8} + \dots$$

$$b_{06}^{(5)} = -\frac{1}{616\sigma^6} - \frac{3}{77\sigma^7} - \frac{1467}{2464\sigma^8} + \dots$$

$$b_{16}^{(5)} = -\frac{1}{1584} + \frac{1}{1848\sigma} + \frac{7}{1056\sigma^2} + \frac{337}{88704\sigma^3} + \frac{53}{1848\sigma^4} + \frac{51433}{315392\sigma^5} + \frac{2188103}{2064384\sigma^6} + \frac{471762913}{60555264\sigma^7} + \frac{4428495037}{69206016\sigma^8} + \dots$$

$$b_{36}^{(5)} = -\frac{1}{84} + \frac{10}{231\sigma} - \frac{17}{924\sigma^2} + \frac{103}{3168\sigma^3} + \frac{2489}{14784\sigma^4} + \frac{236615}{236544\sigma^5} + \frac{38344237}{5677056\sigma^6} + \frac{776232845}{15138816\sigma^7} + \frac{52467158027}{121110528\sigma^8} + \dots$$

$$b_{56}^{(5)} = \frac{1207}{55440} - \frac{661}{9240\sigma} + \frac{17}{12320\sigma^2} - \frac{5525}{88704\sigma^3} - \frac{1169}{3520\sigma^4} - \frac{9116467}{4730880\sigma^5} - \frac{131486063}{10321920\sigma^6} - \frac{1918435847}{20185088\sigma^7} - \frac{639291980689}{807403520\sigma^8} + \dots,$$

$$\tag{78}$$

and for a random system, as for the lower orders, $\overline{B_k^{(5)}} = b_{k0}^{(0)}$.

V. DISCUSSION

The above derived formulas despite their hefty look are very practical. Indeed, they present the nonlinear initial susceptibilities of a superparamagnetic particulate medium as analytical expressions of arbitrary accuracy. With respect to the frequency dependence they give the exact full structure of the susceptibility and prove that it is very simple thus putting former intuitive considerations on a solid ground. This makes our formulas a handy tool for asymptotic analysis. Yet more convenient they are for numerical work because with their use the difficult and time-consuming procedure of solving the differential equations is replaced by a plain summation of certain power series. For example, if to employ Eqs. (72)–(78), a computer code that fits simultaneously experimental data on linear and a set of nonlinear susceptibilities taking into account the particle polydispersity of any kind (easy axes directions, activation volume, anisotropy constants) becomes a very fast procedure.

Graphic examples justifying our claims are presented in Figs. 5 and 6, where the components of two nonlinear complex susceptibilities are plotted as the functions of the parameter σ. For a given sample, σ in a natural way serves as a dimensionless inverse temperature. In those figures, the solid lines correspond to the above-proposed asymptotic formulas where we keep the terms up to σ^{-3}. The circles show the results of numerically-exact solutions obtained by the method described in Ref. 6. Note that even at $\sigma \sim 5$ the accuracy is still rather high.

The model that may be called the predecessor of the afore-derived results was proposed in Ref. 23. There, the authors calculated the initial susceptibilities up to the seventh order having replaced a superparamagnetic assembly by a two-level macrospin system. The interrelation between the present work and Ref. 23 closely resembles the situation with the evaluation of the rate of a superparamagnetic process. First in 1949 Néel[1] and then, ten years later, Brown[3] had evaluated the superparamagnetic time in the framework of a two-level model. In such a framework, one allows for the magnetic moment flips but totally neglects its possible diffusion over energetically less-favorable directions. In 1963 Brown[4] had succeeded to overcome this artificial assumption and took into account the possibility for the magnetic moment to wander over all 4π radians.

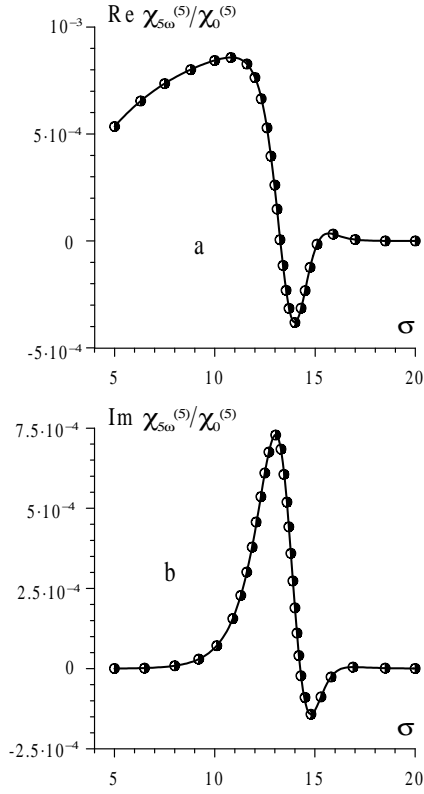In the present case, the obtained v/T dependencies of

FIG. 6: Real (a) and imaginary (b) components of the fifth-order susceptibility of a random superparamagnetic assembly; the dimensionless frequency is $\omega\tau_0 = 10^{-6}$. Solid lines show the proposed asymptotic formulas with the accuracy σ^{-3}, circles present the result of a numerical evaluation

the nonlinear susceptibilities and those from Ref. 23 are qualitatively the same. Their most typical feature is the double-peak shape. Quantitatively, however, the corresponding lines differ and do not reduce to one another in any case. Indeed, as long as the temperature is finite (whatever low), the configurational space for the unit vector $\boldsymbol{e}$ of the magnetic moment is the full (4π-radian) solid angle; its reduction to just two directions along a bidirectional axis could not be done otherwise than "by hand". This is exactly what the two-level Ising-like model does: it forcibly imparts a quantum property (discrete spin projections) to a macrospin assembly. From the calculational viewpoint, another essential demerit of the results[23] is that the coefficients in the susceptibility formulas are not

given in an analytic form. The authors propose to evaluate them by solving an infinite set of recurrence equations. Hence, the procedure[23] does not provide any gain with respect to former ones neither in analytical considerations nor in constructing fitting codes.

In the presented framework the results by Klik and Yao (including the analytical formulas for them missing in Ref. 23) can be obtained immediately if to take the function φ_1 in a step-wise form (23) and not to allow for the corrections caused by the finiteness of its derivative at $x = 0$. In our terms this means to stop at set (45), i.e., "zero-derivative" solution, and not to go further. The emerging error is however, uncontrollable and not at all small. As an illustration, in Fig. 5 we show the result obtained with this model (dashed lines) for the cubic susceptibility $\chi_{3\omega}^{(3)}$ in a textured system where the particle common axis $\boldsymbol{n}$ is tilted under the angle $\beta = \pi/3$ to the probing field. One can see that deviations are substantial.

In Ref. 6 we have proposed, although without rigorous justification, a formula for the cubic susceptibility of a random assembly

$$\chi_{3\omega}^{(3)} = -\frac{1}{4}\chi_0^{(3)}\frac{(1 + 2S_2^2)(1 - i\omega\tau_1)}{45(1 + i\omega\tau_1)(1 + 3i\omega\tau_1)}, \qquad (79)$$

that proved to be well adjusted for approximating the results of numerical calculations in all the temperature interval and also appeared to be good for fitting experimental data.[7] Now we see that this very expression follows from Eqs. (73)–(75) if to expand the coefficients $b_{i0}^{(3)}$ up to the zeroth order with respect to σ^{-1}. This justifies Eq. (79) as a formula yielding a correct frequency dispersion of the cubic susceptibility of a random assembly at low temperatures. The cause of its applicability at high temperatures is the exponential dependence of τ_1 on σ. Indeed, in the frequencies range $\omega\tau_0 \ll 1$, where we work, the condition $\sigma \lesssim 1$ means $\tau_1 \to \tau_0$, and all the dispersion factors in Eq. (79) drop out. This transforms expression (79) in a correct static susceptibility that is also a true result. To avoid any confusion we remark that Eq. (79) differs from formula for $\chi_{3\omega}^{(3)}$ given in Ref. [6] by the coefficient $(-1/45)$ due to the difference in definitions: in Ref. [6] it was included in $\chi_0^{(3)}$.

Applying the similar procedure to Eqs. (76)–(78) we get the expression for the fifth-order susceptibility

$$\chi_{5\omega}^{(5)} = \frac{1}{16}\chi_0^{(5)}\frac{(2 + 12S_2^2 + 4S_2^3)}{945}\frac{1 - \frac{21}{8}i\omega\tau_1 - \frac{3}{4}\omega^2\tau_1^2}{(1 + i\omega\tau_1)(1 + 3i\omega\tau_1)(1 + 5i\omega\tau_1)}, \qquad (80)$$

that, following the example of the already tested Eq. (79), has high chances to be a good approximation for $\chi_{5\omega}^{(5)}$

in the whole temperature interval. As we have already ascertained in Ref. [6], the best interpolation expression

for the relaxation time in the susceptibility formulas is

$$\tau_1 = \tau_D \frac{e^\sigma - 1}{2\sigma} \left[\frac{\sigma}{1+\sigma} \sqrt{\frac{\sigma}{\pi}} + 2^{-\sigma-1} \right]^{-1},$$

proposed in Refs. [13, 14].

VI. CONCLUSIONS

A consistent procedure yielding the integral relaxation time and initial nonlinear susceptibilities for an assembly of non-interacting superparamagnetic particles is constructed in the low-to-moderate temperature range. Starting from the micromagnetic kinetic equation that describes intrinsic rotary diffusion of the particle magnetic moment, we obtain the results in an analytical form. They are presented as asymptotic series with respect to the dimensionless parameter σ that is the uniaxial anisotropy barrier height scaled with temperature. High-order expansion terms are easily accessible that allows to achieve any desirable extent of accuracy. This is proven by comparison of the proposed approximation with the numerically-exact results. The susceptibilities contain angular dependencies that allow one to consider the particle assemblies with any extent of orientational texture—from perfectly aligned to random. The new formulas stand closer to reality than those for a two-level system and are to facilitate considerably both analytical and numerical calculations in the theory of superparamagnetic relaxation in single-domain particles.

Acknowledgments

APPENDIX A: EVALUATION OF THE EXPANSION COEFFICIENTS FOR EIGENFUNCTIONS ψ_0 AND ψ_1

Both functions ψ_0 and ψ_1 are uniaxially symmetrical about the anisotropy axis $\boldsymbol{n}$ and can be expanded in the Legendre polynomial series, see Eq. (32):

$$\psi_0 = \tfrac{1}{2} \sum_{k=0} (2k+1) S_k P_k(x), \quad k = 0, 2, 4, \ldots, \quad (A1)$$
$$\psi_1 = \tfrac{1}{2} \sum_{k=1} (2k+1) Q_k P_k(x), \quad k = 1, 3, 5, \ldots,$$

where in accordance with the parity properties of the eigenfunctions non-zero terms are

$$S_0 = 1, \quad S_k = \big(P_k(x) \big| \psi_0\big), \quad k = 2, 4, \ldots, \quad (A2)$$
$$Q_k = \big(P_k(x) \big| \psi_1\big), \quad k = 1, 3, 5, \ldots.$$

Taking into account that $\psi_1 = \psi_0 \varphi_1$, where ψ_0 in a finite form is given by Eq. (11), one arrives at the general formula

$$\mathcal{F}_k = (1/R) \int_0^1 P_k(x) e^{\sigma x^2}\, dx, \quad (A3)$$

where $\mathcal{F}$ is S_k for even and is Q_k for odd values of the index, and the function $R(\sigma)$ is defined by Eq. (11). In particular

$$Q_1 = (1/R) \int_0^1 x e^{\sigma x^2}\, dx = \tfrac{1}{2}(e^\sigma - 1)/\sigma R. \quad (A4)$$

Using asymptotic expansion (12) for R, one gets

$$Q_1 = 1/G = 1 - \frac{1}{2\sigma} - \frac{1}{2\sigma^2} - \frac{5}{4\sigma^3} - \frac{37}{8\sigma^4} - \frac{353}{16\sigma^5} - \frac{4881}{32\sigma^6} - \frac{55205}{64\sigma^7} - \frac{854197}{128\sigma^8} + \ldots \quad (A5)$$

Knowing Q_1, one can derive all the other moments Q_k with the aid of the three-term recurrence relation obtained from Eq. (8) by setting there $b_k = Q_k$ and $\lambda = 0$. The same relation can be used to find the equilibrium order parameters S_k. This is a head-to-tail procedure, where $S_0 = 1$ and S_2 is determined by the integral

$$S_2 = (1/2R) \int_0^1 \left(3x^2 - 1\right) e^{\sigma x^2} dx. \quad (A6)$$

Taking the latter by parts one gets

$$S_2 = \tfrac{3}{4} \left[e^\sigma - R\right]/\sigma R.$$

On comparison with Eq. (A4), we find

$$S_2 = \tfrac{3}{2} Q_1 - \tfrac{3}{4} (3 - 2\sigma)/\sigma,$$

that upon substituting asymptotic series (A5), transforms into

$$S_2 = 1 - \frac{3}{2\sigma} - \frac{3}{4\sigma^2} - \frac{15}{8\sigma^3} - \frac{111}{16\sigma^4} - \frac{1059}{32\sigma^5} - \frac{12243}{64\sigma^6} - \frac{165615}{128\sigma^7} - \frac{2562591}{256\sigma^8} + \dots \qquad (A7)$$

APPENDIX B: EVALUATION OF THE CORRECTING COEFFICIENTS D_n IN A GENERAL CASE

Let us present the solution of Eq. (42) in the form

$$f_1^{(n)} = \psi_0 g_1^{(n)} + u^{(n)}, \qquad (B1)$$

where the functions $g_1^{(n)}$ are rendered by formulas (45) and are not corrected with respect to the derivative $d\varphi_1/dx$. Substituting Eq. (B1) in (42) and taking into account Eqs. (45), we get a recurrence sequence of equations for the corrections $u^{(n)}$:

$$\widehat{L}\, u^{(n)} = \widehat{V}\, u^{(n-1)} + \widehat{J}\psi_0 \frac{(\boldsymbol{e}\cdot\boldsymbol{h})^n}{n!} \widehat{J}\varphi_1. \qquad (B2)$$

With allowance for the fact that function $\varphi_1^{(0)}$ depends only on x, Eq. (B2) rewrites as

$$\widehat{L}\, u^{(n)} = \widehat{V}\, u^{(n-1)} + \frac{d}{dx}\left[\psi_0(1-x^2) \frac{(\boldsymbol{e}\cdot\boldsymbol{h})^n}{n!} \frac{d\varphi_1}{dx} \right].$$

Finally, making use of the relation

$$\frac{d\varphi_1}{dx} = \frac{\lambda_1}{2\psi_0(1-x^2)}, \qquad (B3)$$

that follows from Eq. (18), we get

$$\widehat{L}\, u^{(n)} = \widehat{V}\, u^{(n-1)} + \frac{\lambda_1}{2}\frac{d}{dx}\left[\frac{(\boldsymbol{e}\cdot\boldsymbol{h})^n}{n!} \right]. \qquad (B4)$$

In particular, at $n = 1$ Eq. (B4) takes the form

$$\widehat{L}\, u^{(1)} = \frac{\lambda_1}{2}\frac{d}{dx}(\boldsymbol{e}\cdot\boldsymbol{h}) \qquad (B5)$$

Equations (B4) are solved sequentially beginning from Eq. (B5) by expanding in a power series with respect to x. The right-hand sides of Eqs. (B4) and (B5) are proportional to an exponentially small parameter λ_1. Just due to that we did not take into account the corrections of the order $u^{(n)}$ when deriving Eqs. (45). However, the quantities

$$D_n = \left(\varphi_1\big|u^{(n)}\right) \qquad n = 2, 4.., $$

have finite values. To show that, let us multiply Eq. (B4) by φ_1 and integrate. This yields

$$\left(\varphi_1\big|\widehat{L}\, u^{(n)}\right) = \left(\varphi_1\big|\widehat{V}\, u^{(n-1)}\right) + \frac{\lambda_1}{2}\left(\varphi_1\big|\frac{d}{dx}\left[\frac{(\boldsymbol{e}\cdot\boldsymbol{h})^n}{n!}\right]\right). \qquad (B6)$$

In the left part we make use of the fact that φ_1 is the left eigenfunction of the operator $\widehat{L}$, in the right part the integrals are taken by parts and yield

$$\lambda_1 D_n = 2\int_0^1 (1-x^2)u^{(n-1)}\left[\frac{d\varphi_1}{dx}\right]\frac{d}{dx}(\boldsymbol{e}\cdot\boldsymbol{h})\, dx \quad (B7)$$
$$-\lambda_1 \int_0^1 \frac{d\varphi_1}{dx}\frac{(\boldsymbol{e}\cdot\boldsymbol{h})^n}{n!}\, dx.$$

Replacing the derivative $d\varphi_1/dx$ in the first term of the right-hand side with the aid of Eq. (B3), we arrive at the representation of the coefficient D_n as

$$D_n = \int_0^1 \frac{u^{(n-1)}}{\psi_0}\frac{d}{dx}(\boldsymbol{e}\cdot\boldsymbol{h})dx - \int_0^1 \frac{d\varphi_1}{dx}\frac{(\boldsymbol{e}\cdot\boldsymbol{h})^n}{n!}dx. \quad (B8)$$

Since $\psi_0 \propto \exp(\sigma x^2)$, the first integral in Eq. (B8) can be presented as an asymptotic series if the power expansion of the function $u^{(n-1)}$ in the vicinity of $x = 0$ is known. A closed form for the second integral can be found with the aid of the table given in Eq. (51), see section III A.

As an example, we calculate the coefficient D_2. As from the addition theorem

$$(\boldsymbol{e}\cdot\boldsymbol{h}) = \cos\theta\cos\beta + \sin\theta\sin\beta\cos\varphi,$$

we seek the solution of Eq. (B5) the sum

$$u^{(1)} = \cos\beta \sum_k C_k^{(0)} x^k + \sin\beta e^{i\varphi}(1-x^2)^{\frac{1}{2}} \sum_k C_k^{(1)} x^k. \qquad (B9)$$

Here the upper index of the C coefficients corresponds to the azimuthal number m of the spherical harmonic $e^{im\varphi}$. Operator $\widehat{L}$ now includes the azimuthal coordinate and takes the form

$$-\widehat{L} = (1-x^2)\frac{d}{dx^2} - \left[2\sigma x(1-x^2) + 2x\right]\frac{d}{dx}$$
$$+ \left[2\sigma(3x^2-1) - \frac{m^2}{1-x^2}\right].$$

Substitution of expansion (B9) in Eq. (B5) leads to the set of equations

$$2\sigma(k+m+1)C_{k-2}^{(m)} - [k(k+1+2m+2\sigma) + m(m+1) + 2\sigma]\, C_k^{(m)} + (k+1)(k+2)C_{k+2}^{(m)} = N_k^{(m)}, \tag{B10}$$

where $m = 0, 1$ and the numbers in the right-hand side are

$$N_k^{(0)} = \begin{cases} -1 & \text{for } k = 0, \\ 0 & \text{for } k \neq 0, \end{cases} \qquad N_k^{(1)} = \begin{cases} 1, & \text{for } k \text{ odd,} \\ 0, & \text{for } k \text{ even.} \end{cases}$$

In reality, one retains in expansion (B9) only a finite number of terms so that Eqs. (B10) could be easily solved analytically by any computer algebra solver. In terms of expansion (B9) expression (B8) at $n = 2$ writes

$$D_2 = \cos^2 \beta \sum_{k=0} C_{2k}^{(0)} \frac{(2k-1)!!}{2^k \sigma^k G} \tag{B11}$$

$$-\frac{1}{2}\sin^2 \beta \sum_{k=1} C_{2k-1}^{(1)} \frac{(2k-1)!!}{2^k \sigma^k G}$$

$$-\frac{1}{6} - \frac{2G-3}{6G} P_2(\cos \beta).$$

Since the coefficients C found from Eq. (B10) are functions of σ, one has to perform in Eq. (B11) asymptotic expansion. This gives finally

$$D_2 = \frac{1}{4\sigma} + \frac{1}{4\sigma^2} + \frac{5}{8\sigma^3} + \frac{37}{16\sigma^4} + \dots \tag{B12}$$

$$-\sin^2 \beta \left(\frac{1}{4} + \frac{1}{8\sigma} + \frac{1}{16\sigma^2} + \frac{7}{64\sigma^3} + \frac{19}{64\sigma^4} + \dots \right).$$

As it should be, at $\beta = 0$ this formula reduces to Eq. (52) that was obtained for a one-dimensional case. We remark, however, that in a tilted situation ($\beta \neq 0$) the coefficient D_2 acquires a contribution independent on σ that assumes the leading role. This effect is clearly due to admixing of transverse modes to the set of eigenfunctions of the system, and it is just it that causes so a significant discrepancy between the "zero-derivative" approximation and the correct asymptotic expansion for $\chi^{(3)}$ curves in Fig. 5. Evaluation of the coefficient D_4 is done according to the same scheme and requires taking into account a number of the perturbation terms that makes it rather cumbersome.

APPENDIX C: EVALUATION OF INTEGRALS

Before proceeding to the integrals (scalar products) in Eqs. (62)–(66) and (68), let us consider the "primitive" ones

$$X_n = \left((\boldsymbol{e} \cdot \boldsymbol{h})^n | \psi_0 \right), \qquad Y_n = \left((\boldsymbol{e} \cdot \boldsymbol{h})^n | \psi_1 \right).$$

The functions ψ_0 and ψ_1 are originally defined in terms of the angle $\theta = \arccos(\boldsymbol{e} \cdot \boldsymbol{n})$. Thus, before performing integration one needs to transform both integrands to the same set of angles. Doing this with the aid of the addition theorem for Legendre polynomials, one finds

$$X_2 = \tfrac{1}{3}\left[2S_2 P_2(\cos\beta) + 1\right], \qquad X_4 = \tfrac{1}{35}\left[8S_4 P_4(\cos\beta) + 20S_2 P_2(\cos\beta) + 7\right],$$

$$X_6 = \tfrac{1}{231}\left[16S_6 P_6(\cos\beta) + 72S_4 P_4(\cos\beta) + 110S_2 P_2(\cos\beta) + 33\right], \tag{C1}$$

and

$$Y_1 = Q_1 \cos\beta, \qquad Y_3 = \tfrac{1}{5}\left[2Q_3 P_3(\cos\beta) + 3Q_1 \cos\beta\right],$$

$$Y_5 = \tfrac{1}{63}\left[8Q_5 P_5(\cos\beta) + 28Q_3 P_3(\cos\beta) + 27Q_1 \cos\beta\right], \tag{C2}$$

where $\cos\beta = (\boldsymbol{n} \cdot \boldsymbol{h})$ and the parameters S_k and Q_k are the expansion coefficients introduced by formulas (32).

Now using the expressions for functions $f_0^{(n)}$ and $f_1^{(n)}$ derived in Sec. III A one sees that the relevant integrals of Eqs. (63)–(68) are expressed in terms of X_k and Y_k as

$$\left((\boldsymbol{e} \cdot \boldsymbol{h}) | f_0^{(1)} \right) = X_2, \quad \left((\boldsymbol{e} \cdot \boldsymbol{h}) | f_0^{(3)} \right) = \tfrac{1}{6}X_4 - \tfrac{1}{2}X_2^2, \quad \left((\boldsymbol{e} \cdot \boldsymbol{h}) | f_0^{(5)} \right) = \tfrac{1}{120}X_6 - \tfrac{1}{8}X_4 X_2 + \tfrac{1}{4}X_2^3; \tag{C3}$$

$$\left(\varphi_1 | f_0^{(1)} \right) = Y_1, \quad \left(\varphi_1 | f_0^{(3)} \right) = \tfrac{1}{6}Y_3 - \tfrac{1}{2}X_2 Y_1, \quad \left(\varphi_1 | f_0^{(5)} \right) = \tfrac{1}{120}Y_5 - \tfrac{1}{12}Y_3 X_2 + \tfrac{1}{4}X_2^2 Y_1 - \tfrac{1}{24}X_4 Y_1; \tag{C4}$$

$$\left(\varphi_1\big|f_1^{(2)}\right) = \tfrac{1}{2}X_2 - Y_1^2 + D_2 , \quad \left((\boldsymbol{e}\cdot\boldsymbol{h})\big|f_1^{(2)}\right) = \tfrac{1}{2}Y_3 - Y_1 X_2 + D_2 Y_1 ,$$

$$\left(\varphi_1\big|f_1^{(4)}\right) = \tfrac{1}{24}X_4 - \tfrac{1}{3}Y_3 Y_1 + \tfrac{1}{2}X_2 Y_1^2 + D_4 + D_2\left(\varphi_1\big|f_1^{(2)}\right) ,$$

$$\left((\boldsymbol{e}\cdot\boldsymbol{h})\big|f_1^{(4)}\right) = \tfrac{1}{24}Y_5 - \tfrac{1}{6}Y_3 X_2 - \tfrac{1}{6}X_4 Y_1 + \tfrac{1}{2}X_2^2 Y_1 + D_4 Y_1 + D_2\left((\boldsymbol{e}\cdot\boldsymbol{h})\big|f_1^{(2)}\right) . \tag{C5}$$

[1] L. Néel, Ann. Geophys. **5**, 99 (1949) ; C. R. Acad. Sci. (Paris) 228, 664 (1949).

[2] T. Bitoh, K. Ohba, M. Takamatsu, T. Shirane, and S. Chikazawa, J. Phys. Soc. Japan **64**, 1311 (1995); J. Magn. Magn. Mater. 154, 59 (1996).

[3] W.F. Brown (Jr.), J. Appl. Phys. **30**, Suppl.5, 130S (1959).

[4] W.F. Brown (Jr.), Phys. Rev. **130**, 1677 (1963).

[5] J.-L. Dormann, D. Fiorani, and E. Tronc, Adv. Chem. Phys. **98**, 283 (1997).

[6] Yu.L. Raikher and V. I. Stepanov, Phys. Rev. B **55**, 15005 (1997).

[7] L. Spinu, D. Fiorani, H. Srikanth, F. Lucari, F. D'Orazio, E. Tronc, M. Nogués, J. Magn. Magn. Mater. **226–230**, 1927 (2001).

[8] B.A. Storonkin, Kristallografiya **30**, 841 (1985) [Sov. Phys. Crystallography **30**, 489 (1985)].

[9] A. Aharoni, Phys. Rev. **135A**, 447 (1964).

[10] Yu.P. Kalmykov, Phys. Rev. E **61**, 6320 (2000).

[11] L. Bessias, L. BenJaffel, and J.-L. Dormann, Phys. Rev. B **45**, 7805 (1992).

[12] A. Aharoni, Phys. Rev. B **46**, 5434 (1992).

[13] W.T. Coffey, P.J. Cregg, D.S.F. Crothers, J.T. Waldron, and A. W. Wickstead, J. Magn. Magn. Mater. **131** (1994) L301.

[14] P.G. Cregg, D.S.F. Crothers, and A.W. Weakstead, J. Appl. Phys. **76**, 4900 (1994).

[15] W.F. Brown (Jr.), Physica B **86–88**, 1423 (1977).

[16] W. F. Brown (Jr.), IEEE Trans. Magn. **15**, 1196 (1979).

[17] Yu.L. Raikher and M.I. Shliomis, Zh. Eksp. Teor. Fiz. **67**, 1060 (1974) [Sov. Phys. JETP **40**, 526 (1974)]

[18] W.T. Coffey, Adv. Chem. Phys. **103**, 259 (1998).

[19] D.A. Garanin, V.V. Ishchenko, and L.V. Panina, Teor. Mat. Fiz. **82**, 242 (1990) [Theor. Math. Phys. **82**, 169 (1990)].

[20] W. T. Coffey, D.S.F. Crothers, Yu.P. Kalmykov, E.S. Massawe, and J.T. Waldron, Phys. Rev. E **49**, 1869 (1994);

[21] W.T. Coffey and D.S.F. Crothers, Phys. Rev. E **54**, 4768 (1996).

[22] W.T. Coffey, Yu.P.Kalmykov, and J.T. Waldron, The Langevin Equation, World Scientific, Singapore, 1996.

[23] I. Klik and Y.D. Yao, J. Magn. Magn. Mater. **186**, 233 (1998).

[24] J. García-Palacios and P. Svedlidh, Phys. Rev. Lett. **85**, 3724 (2000).

[25] We remark that, in principle, there might occur a situation, where τ is very long, i.e., the quality factor of precession is very high. Then the gyromagnetic term in the kinetic equation must be retained so that Larmor precession begins to interact with the superparamagnetic (longitudinal) relaxation. An example of such a situation is considered in Ref. 24, where some interesting nonlinear effects are found.